Cationic Alkylaluminum-Complexed Zirconocene Hydrides as Participants in Olefin-Polymerization Catalysis

Steven M. Baldwin,[†] John E. Bercaw,[*, †] and Hans H. Brintzinger*[,‡]

Contribution from the Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125, USA, and Fachbereich Chemie, Universität Konstanz, D-78457 Konstanz, Germany

E-mail: Bercaw@caltech.edu; Hans.Brintzinger@uni-konstanz.de

Supporting Information

[†] California Institute of Technology
[‡] Universität Konstanz

1. General Experimental Details

All operations were carried out under a protective dinitrogen atmosphere, either in a glovebox or on a vacuum manifold. Phenol was obtained from J. T. Baker and used as obtained. Deuterated solvents were obtained from Cambridge Isotope Laboratories. Tetrachloroethane-d_2 and benzene-d_6 were used as obtained. Toluene was obtained from EMD Chemicals. Toluene (d_8 and d_0) was dried by vacuum transfer from "titanocene".[1] (SBI)$ZrCl_2$ was purchased from Strem Chemicals and used as obtained. $AlMe_3$ and HAl^iBu_2 were used as obtained as neat compounds from Aldrich Chemical Company. $HAlMe_2$ was prepared as reported previously.[2] NMR spectra were obtained using Varian Inova 500 or Mercury 300 spectrometers. Chemical shifts are referenced to residual solvents peaks, 7.00 ppm for the central aromatic proton resonance of toluene and 6.00 ppm for the ^1H signal of tetrachloroethane. Polypropene ^{13}C NMR spectra were referenced to 21.69 ppm for the mmmm pentad of the methyl signal. GPC measurements were conducted, at 160°C and a flow rate of 1 ml/min in 1,2,4-trichlorobenzene, by means of a Polymer Laboratories instrument with three "PLgel Olexis" columns, using either triple detection (refractory index RI, viscosity DP, and light scattering LS15 + LS90) or linear calibration (RI, polyethylene standards).

2. NMR scale reaction of propene with $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$

A 3.1 mM solution of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ was prepared by adding a solution of 1.0 mg (2.2 μmol) of (SBI)$ZrCl_2$ and 7.9 μL (44 μmol, 20 equiv.) of HAl^iBu_2 in 0.7 mL of toluene-d_8 to 2.1 mg (2.3 μmol, 1 equiv.) of $[Ph_3C][B(C_6F_5)_4]$ in a 1 dram vial. The solution was transferred to a J-Young tube and cooled to liquid-nitrogen temperature. From a calibrated gas bulb, 44.3 μmol (20 equiv.) of propene were condensed onto the frozen solution. The tube was warmed to –78°C in a dry ice/acetone bath and the contents mixed at this temperature. The tube was then inserted into an NMR spectrometer cavity thermostated at -30°C. ^1H NMR spectra (8 scans, 2.6 s

acquisition, 10 s delay) were measured immediately after thermal equilibration and then at intervals of 101 seconds. An identical experiment was set up with 88.1 μmol (40 equiv.) of propene. The tube was warmed to −78°C in a dry ice/acetone bath and the contents mixed at this temperature. The tube was then placed in an acetone bath maintained at −30°C for 6 hours after which time the tube was removed and allowed to warm to room temperature. A ^{1}H-NMR spectrum was obtained (Figure S-1) which shows no new alkylaluminum species.

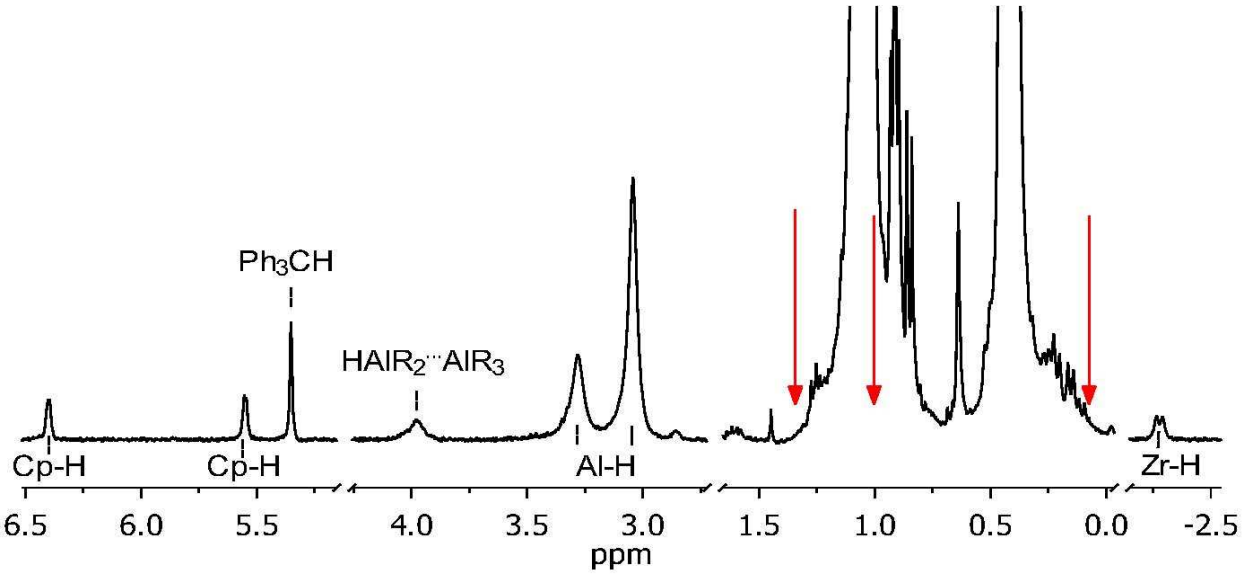

Figure S-1: Room temperature ^{1}H NMR spectra of a toluene-d_8 solution of [(SBI)Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$]$^+$ with 20 equiv. HAl^{i}Bu$_2$ taken after 6 hours at -30°C following addition of 40 equiv. of propene. Position where Al-propyl resonances would appear marked by red arrows.

3. NMR scale reaction of propene with [(SBI)Zr(μ-H)$_3$(AlMe$_2$)$_2$]$^+$

A 3.1 mM solution of [(SBI)Zr(μ-H)$_3$(AlMe$_2$)$_2$]$^+$ was prepared as in section 2, except 2.5 mg HAlMe$_2$ (43 μmol, 20 equiv.) were substituted for the HAl^{i}Bu$_2$. The solution was transferred to a J-Young tube and cooled to liquid-nitrogen temperature. From a calibrated gas bulb, 88.2 μmol (40 equiv.) of propene were condensed onto the frozen solution. The NMR tube was warmed to −78^{o}C in a dry ice/acetone bath and the contents mixed at this temperature. The NMR tube was then inserted into an NMR spectrometer cavity thermostated at -30°C. ^{1}H NMR spectra (1 scan,

10 s acquisition, 0 s delay) were measured immediately after thermal equilibration and then at intervals of 300s. For details of the assignments of the C*H*$_3$-C*H*$_2$-CH$_2$-Al signals observed in this reaction system, see section 5 of the Supporting Information.

4. NMR scale reaction of propene with a mixture of [(SBI)Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$]$^+$ and AlMe$_3$

As in section 2, a 3.1 mM solution of [(SBI)Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$]$^+$ was prepared with 4.0 μL HAl^{i}Bu$_2$ (22 μmol, 10 equiv.). 5.3 μL AlMe$_3$ (55 μmol, 25 equiv.) was added to the J-Young NMR tube and the solution was cooled to liquid-nitrogen temperature. From a calibrated gas bulb, 44.3 μmol (20 equiv.) of propene were condensed onto the frozen solution. The NMR tube was warmed to −78°C in a dry ice/acetone bath and the contents mixed at this temperature. The NMR tube was then inserted into an NMR spectrometer cavity thermostated at -30°C. ^{1}H NMR spectra (8 scans, 2.6 s acquisition, 10 s delay) were measured immediately after thermal equilibration and then at intervals of 300s. Spectra thus obtained are shown in Figure S-2.

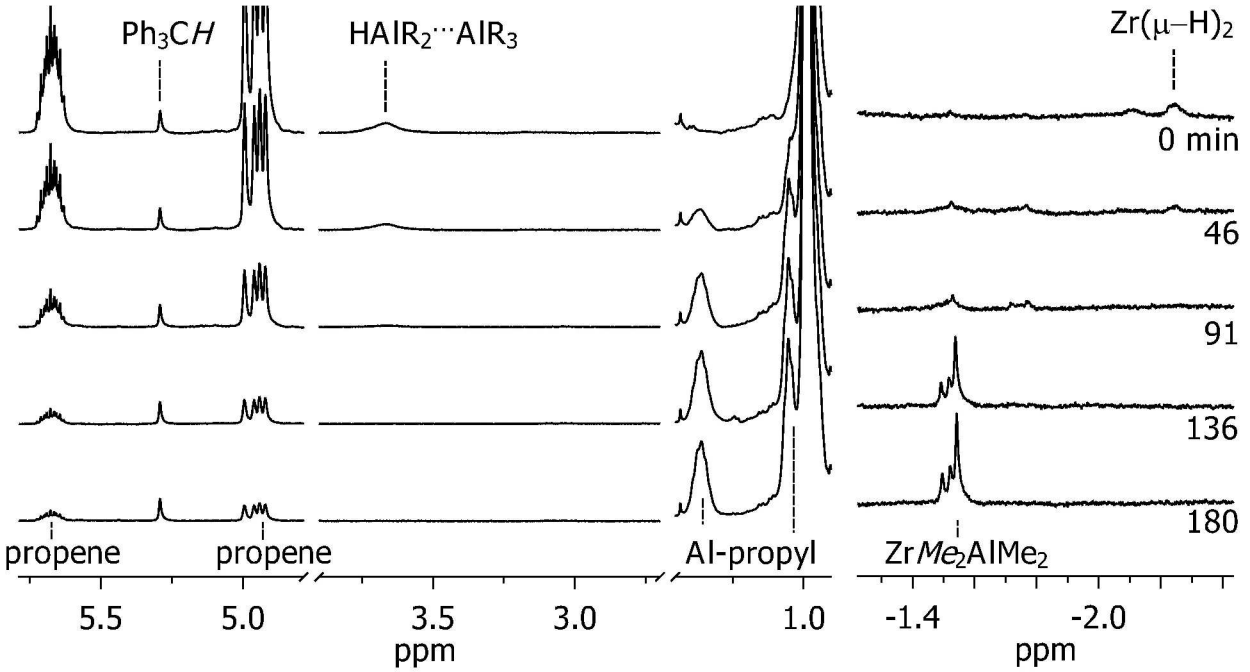

Figure S-2: ^{1}H NMR spectra of a toluene-d_8 solution of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ with 25 equiv. $AlMe_3$ taken immediately (top trace) and 46, 91, 136 and 180 minutes after warming to -30°C in the presence of 20 equiv. propene.

5. Assignment of ^{n}Pr-AlR$_2$

A solution prepared similar to that in section 4 was allowed to warm to room temperature following consumption of all of the propene. One clear new multiplet is observed for the Al-$CH_2CH_2CH_3$ (β-CH_2) at 1.39 ppm while signals for the Al-$CH_2CH_2CH_3$ (α-CH_2) and Al-$CH_2CH_2CH_3$ overlapped with signals from Al-^{i}Bu groups (Figure S-3). A gCOSY was obtained (Figure S-4) which showed that the β-CH_2 signal couples to peaks overlapping with the isobutyl methyl and methylene signals.

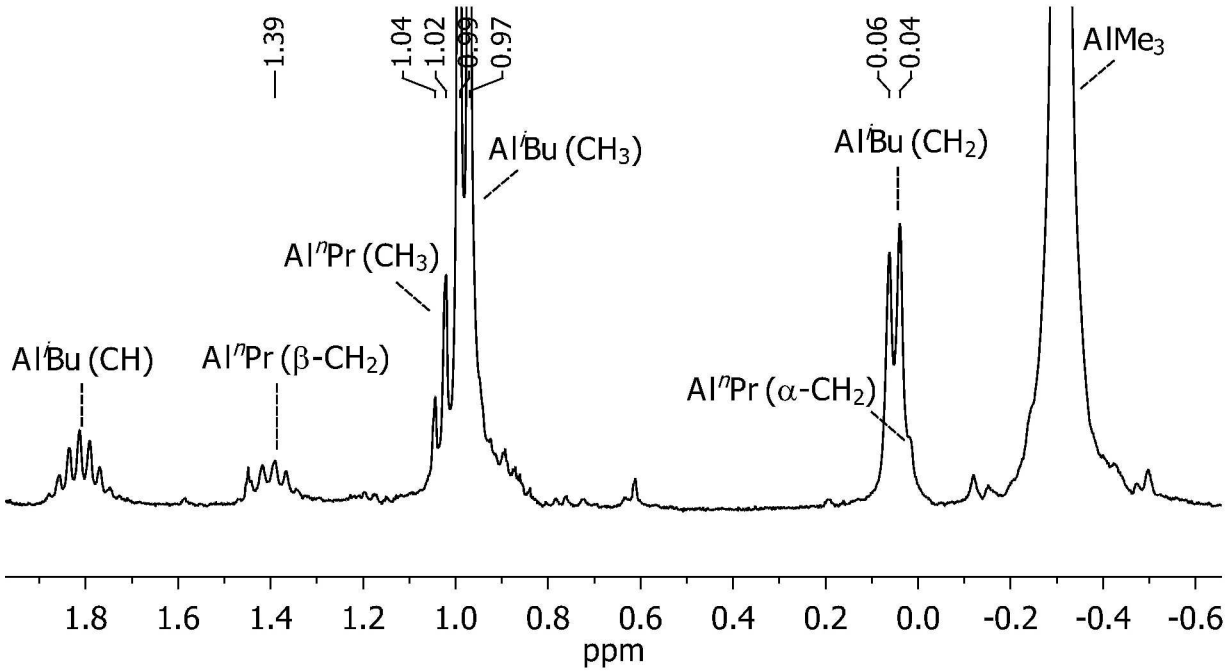

Figure S-3: ^{1}H NMR at 25°C of alkyl region of a solution of $^{n}PrAlR_2$ prepared by reaction of propene with mixture of $[(SBI)Zr(\mu\text{-}H)_3(Al^{i}Bu_2)_2]^+$ and $[(SBI)Zr(\mu\text{-}Me)_2AlMe_2]^+$ at -30°C.

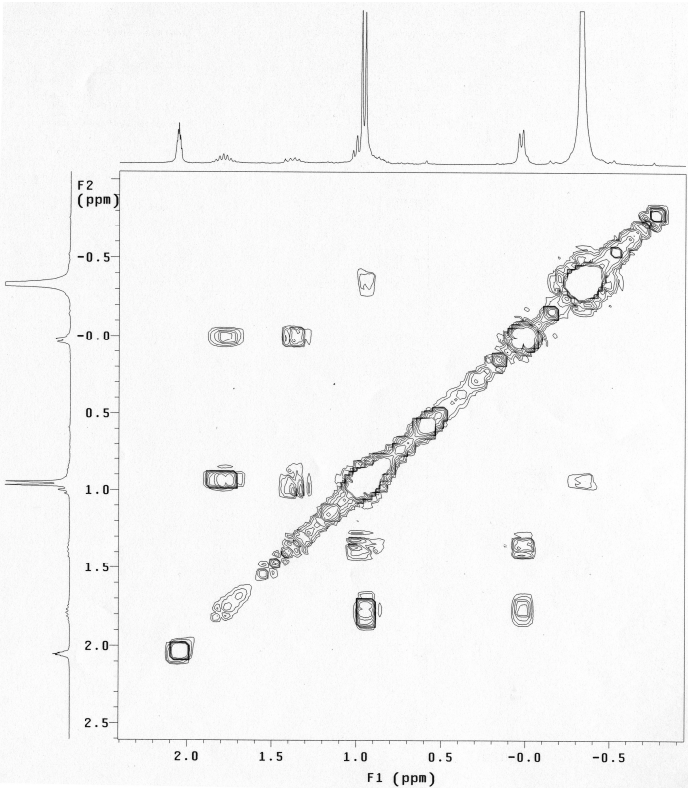

Figure S-4: gCOSY of the sample shown in Figure S-3.

Further evidence for the assignment of the signals to an Al-^{n}Pr was obtained by quenching a sample as described in section 3 with phenol. The sample was allowed to warm to room temperature following consumption of all propene. A J-Young to 14/20 adapter was attached to the top of the J-Young tube and connected to a Schlenk line. Under an Ar flow a solution of 9.2 mg phenol in 0.25 ml C_6D_6 was added to the top of the J-Young valve. Upon opening the valve the vacuum present in the NMR tube pulled the phenol solution into the NMR tube which was cooled to -78°C in a dry ice/acetone bath. The top of the tube was washed with a further 0.1 ml C_6D_6. The tube was closed and shaken resulting in a loss of color, formation of precipitate (presumably $Al(OPh)_3$) and bubbling. A ^{1}H-NMR was obtained (Figure S-5) which clearly showed signals due to propane at 1.27 (spt, $^3J_{HH}$ = 7 Hz) and 0.86 (t, $^3J_{HH}$ = 7 Hz) in addition to signals for excess phenol and CH_4 (not shown).

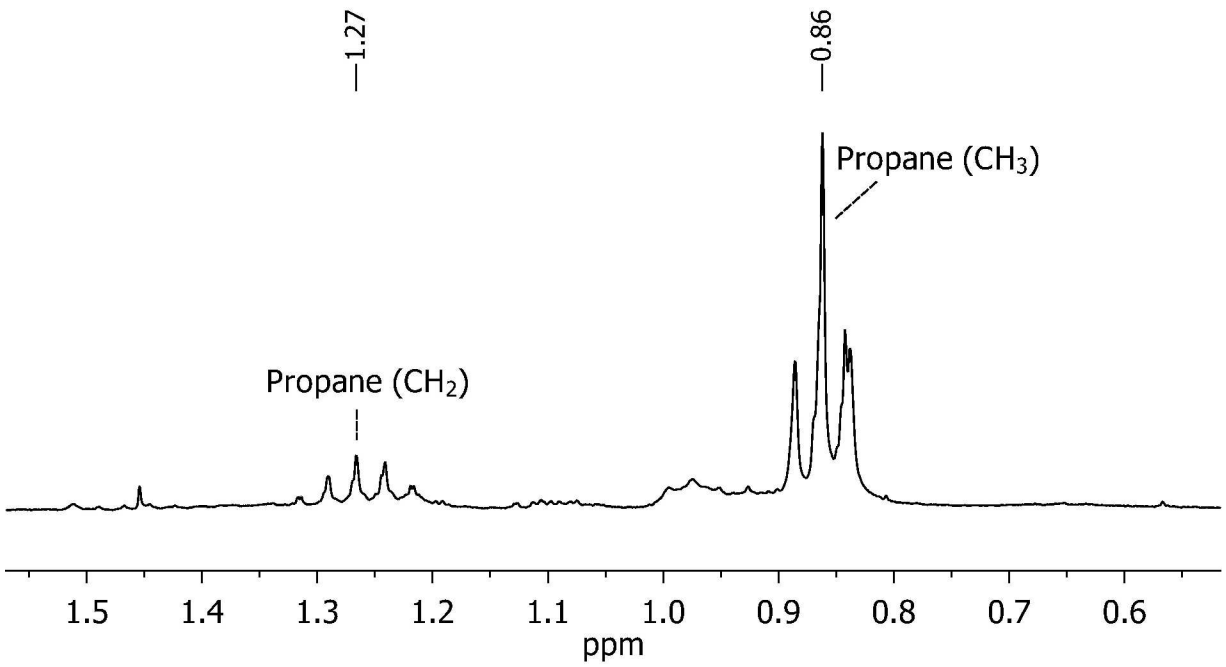

Figure S-5: ^{1}H NMR of sample from polymer solution prepared as in section 3 after being quenched with phenol.

6. Larger scale reaction of propene with $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$

To obtain sufficient polymer for NMR measurements, reactions were conducted on a somewhat larger scale under the same conditions as described above. In a 25-mL side-arm flask a toluene solution containing 10.0 mg (22.3 μmol) of $(SBI)ZrCl_2$, 79.5 μL (446 μmol, 20 equiv.) of HAl^iBu_2 and 20.6 mg (22.3μmol, 1 equiv.) of $[Ph_3C][B(C_6F_5)_4]$ was cooled in liquid nitrogen. From a calibrated gas bulb, 103.66 mL of propene at a pressure of 79 mm Hg (440 μmol, 20 equiv.), was condensed onto the frozen reaction mixture. The flask was warmed to -30°C and stirred at this temperature. After ca. 4 hours, the reaction was quenched by addition of a methanol/HCl mixture and the polymer isolated by filtration and dried overnight at room temperature in a dynamic vacuum. Yield 19.8 mg. Of this polymer, a saturated solution in ca. 0.7 mL of tetrachloroethane-d_2 was prepared at 120°C and ^1H and ^{13}C spectra were taken at this temperature. Another polypropene sample was prepared, under otherwise identical conditions, using a higher ration of [propene]/[Zr] = 40.

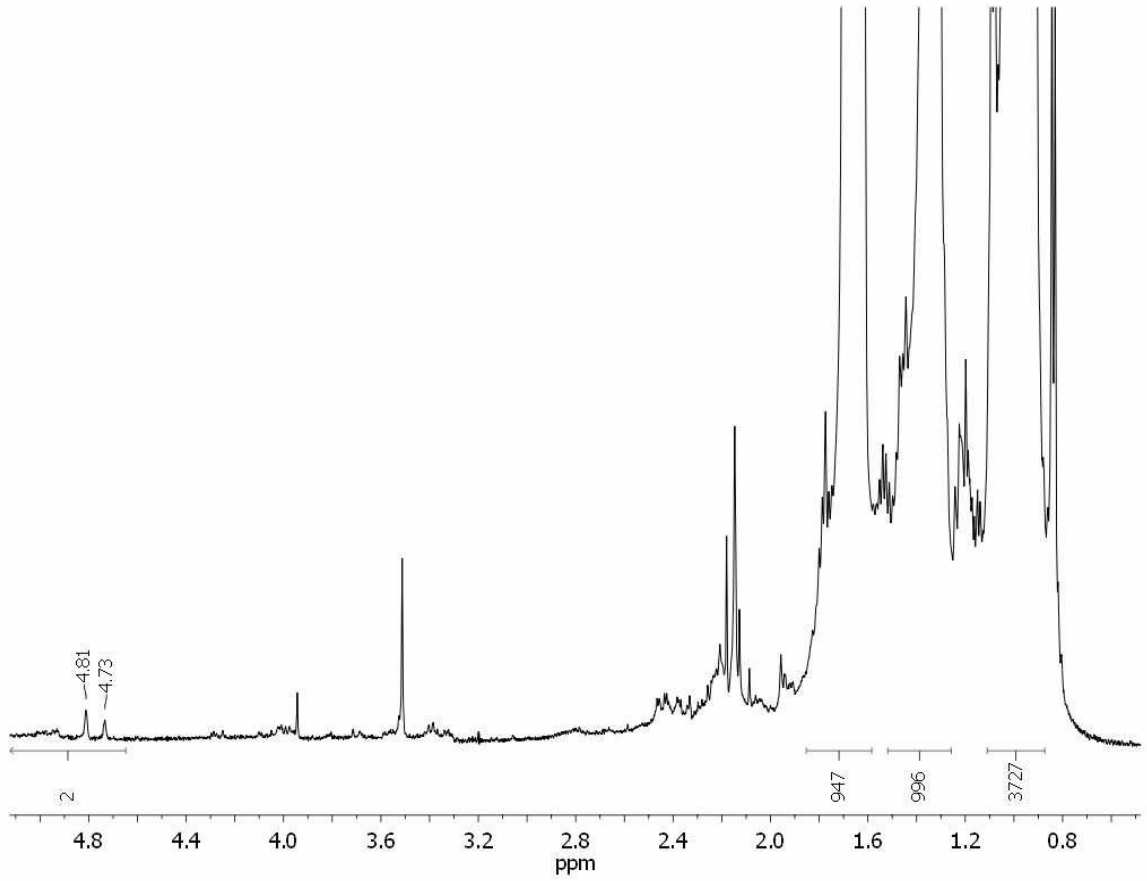

Figure S-6: ^{1}H NMR spectrum of polypropene, obtained in the presence of [(SBI)Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$]$^+$ as described above at [propene]/[Zr] = 20 , in saturated $C_2Cl_4D_2$ solution at 120°C, measured at 500 MHz (64 scans; acquisition 1 s, delay 6s; the signal at 3.5 ppm is due to an impurity in the solvent).

The ^{1}H NMR spectrum was recorded after measuring a ^{13}C NMR spectrum at 120°C for a period of 13 hours. Some isomerization of H_2C=C(Me)-CH$_2$-C(Me)- to H$_3$C-C(Me)=C*H*-C(Me)- must have occurred during this time, as indicated by a broad signal at 4.9-5.0 ppm.

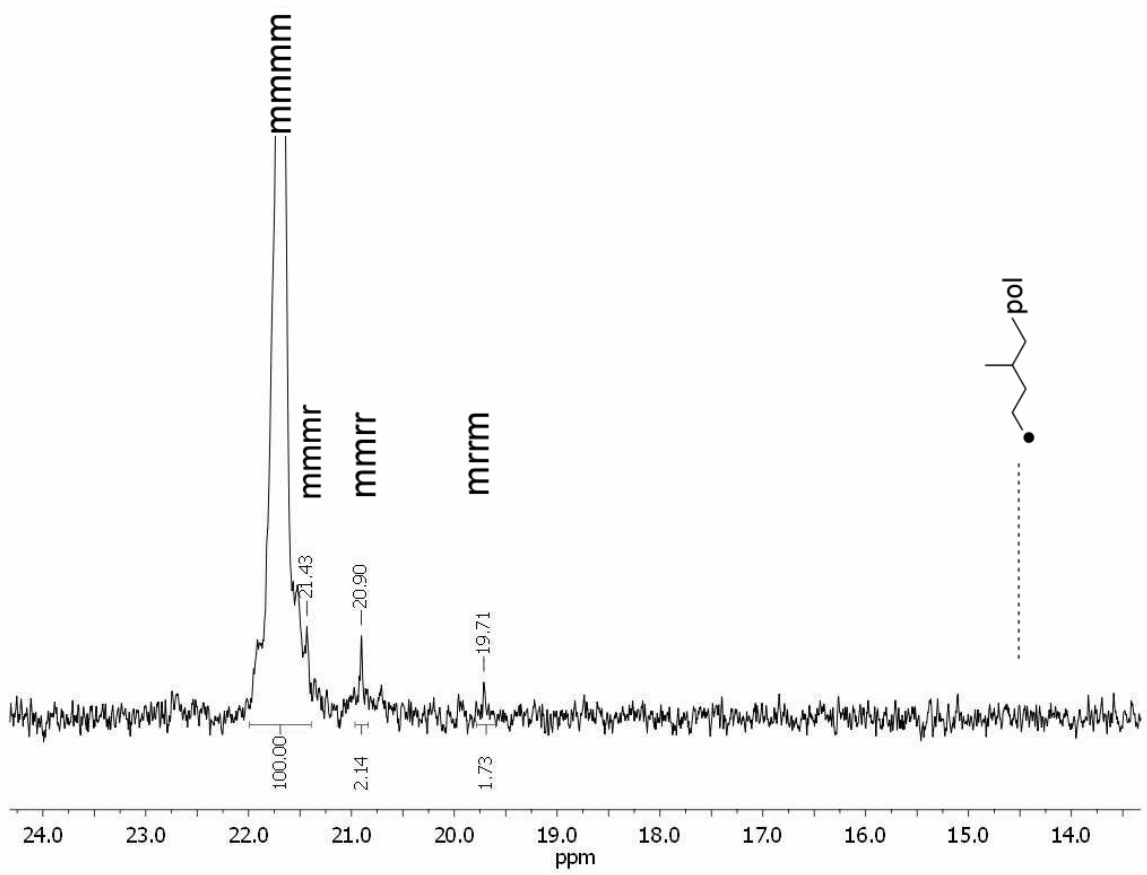

Figure S-7: ^{13}C NMR spectrum of polypropene obtained in the presence of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ as described above at [propene]/[Zr] = 20, in saturated $C_2Cl_4D_2$ solution containing ca. 1 mg/mL of $Cr(acac)_3$ at 120°C, measured at 125.7 MHz (12000 scans, acquisition 3 s, delay 1s).

The polymer is found to be highly isotactic with [mmmm] = 0.94. No end group signals are detectable by ^{13}C NMR. Gel permeation chromatography (GPC) of a polypropene sample, analogously prepared as described above at [propene]/[Zr] = 40, yielded a polydisperity index (PDI) of 1.90 and a number-average molar mass M_n = 78,921 (Figure S-8), equivalent to a mean degree of polymerization P_n = 1880.

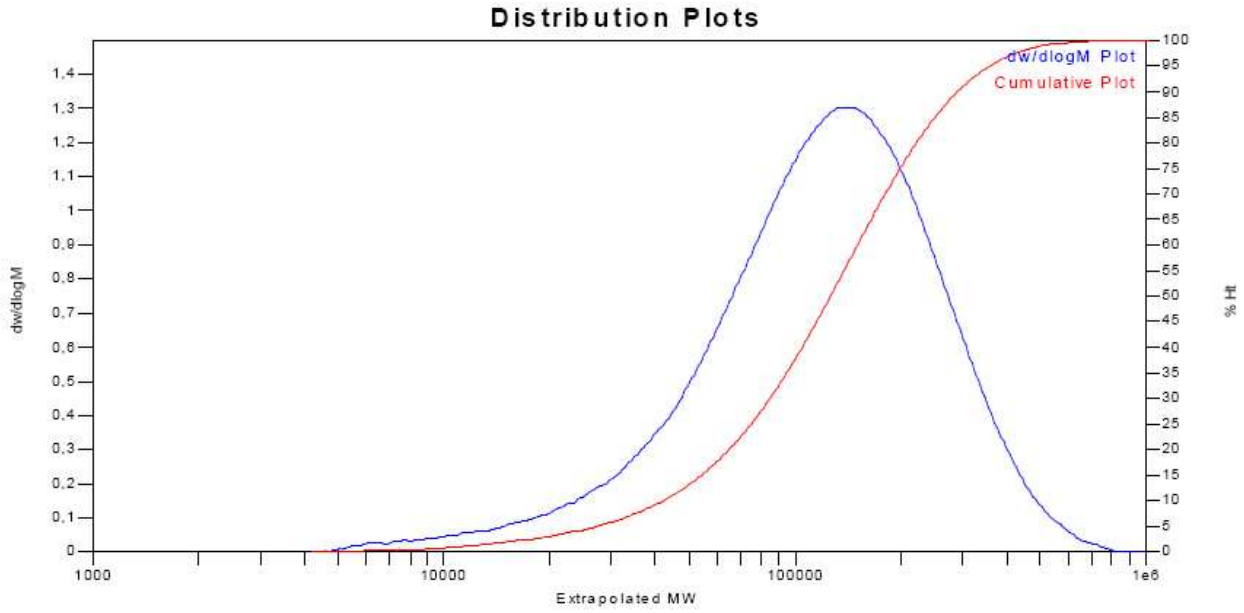

Figure S-8: GPC of polypropene sample prepared from $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ with a propene to Zr ratio of 40:1.

7. Larger scale reaction of propene with a mixture of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ and $AlMe_3$

In analogy to the previous case, a 25-mL side-arm flask, containing a toluene solution of 10.0 mg (22.3 μmol) of $(SBI)ZrCl_2$, 20.6 mg (22.3μmol, 1 equiv.) of $[Ph_3C][B(C_6F_5)_4]$, 39.7 μL (223 μmol, 10 equiv.) of HAl^iBu_2 and 53.4 μL (557 μmol, 25 equiv.) of $AlMe_3$ was cooled in liquid nitrogen and 904 μmol (25 equiv.) of propene were condensed onto the frozen reaction mixture. The flask was warmed to -30°C and stirred at this temperature for ca. 4 hours. After quenching the reaction with methanol/HCl, the polymer was isolated by filtration and dried overnight at room temperature in a dynamic vacuum to yield 29.2 mg of polypropene. Of this polymer, a saturated tetrachloroethane-d_2 solution was prepared at 120°C and ^1H and ^{13}C spectra were taken at this temperature.

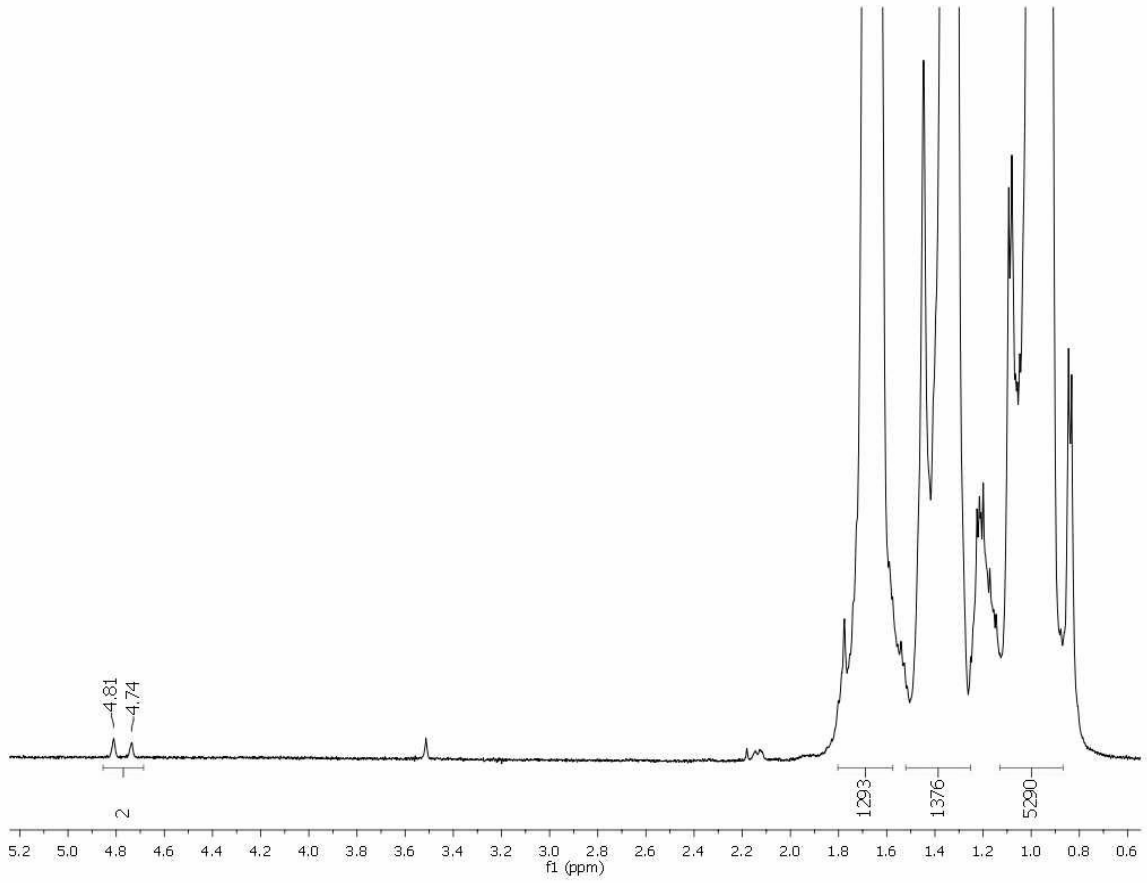

Figure S-9: ^{1}H NMR spectrum of polypropene, obtained in the presence of [(SBI)Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$]$^+$ and AlMe$_3$ *(vide supra)* in $C_2Cl_4D_2$ solution at 120°C, measured at 500 MHz (256 scans, acquisition 1 s, delay 6s; the signal at 3.5 ppm is due to an impurity in the solvent).

Comparison of the combined integral of the H_2C=C signals at 4.74 and 4.81 ppm with that of the main-chain signals indicates that one H_2C=C group is present per 1325 main-chain units.

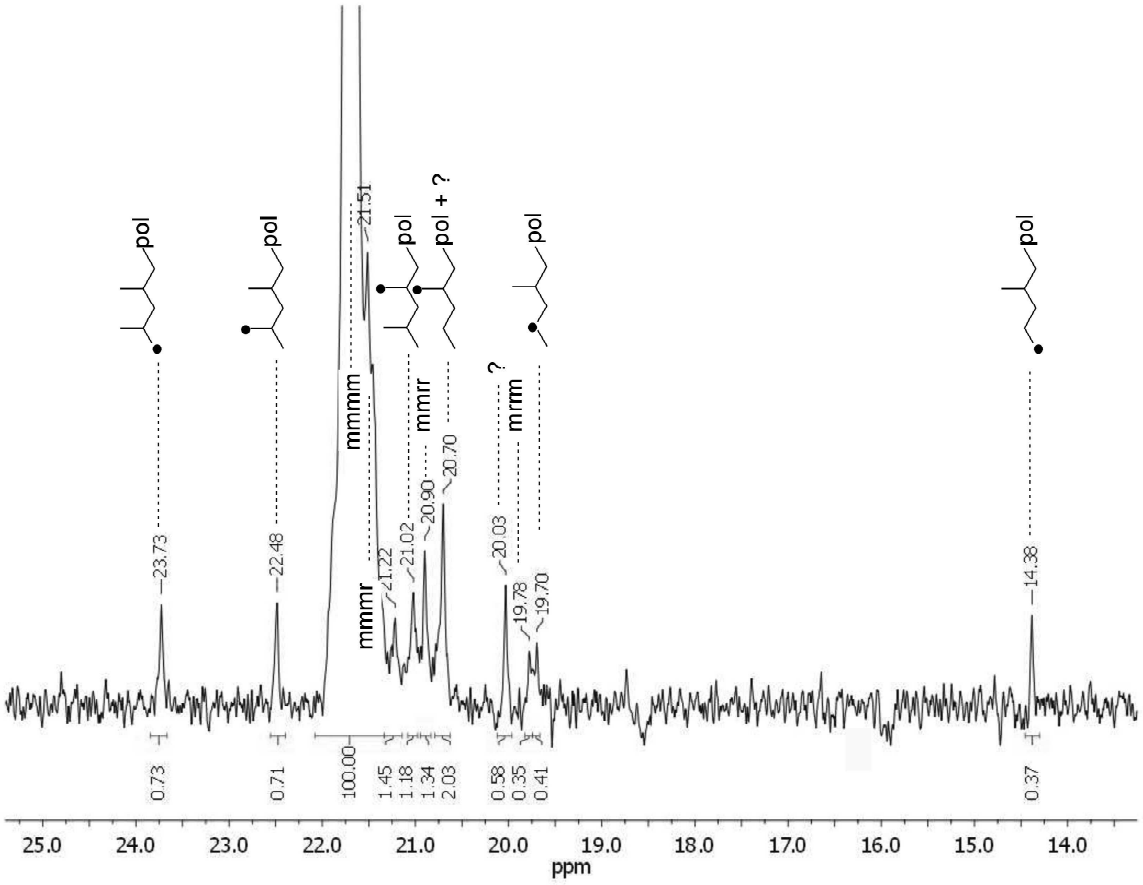

Figure S-10: ^{13}C NMR spectrum of polypropene, obtained in the presence of [(SBI)Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$]$^+$ and AlMe$_3$ *(vide supra)* in $C_2Cl_4D_2$ solution at 120°C, measured at 125.7 MHz (4700 scans, acquisition 3 s, delay 6s).

The polymer is found to be highly isotactic with [mmmm] = 0.97. Most abundant end groups are iso-propyl groups, which arise as chain ends from hydrolysis of AlMe$_2$-capped chains, produced by polymer-vs.-Me exchange between Zr and Al centers and, as a consequence, also as chain starts from propene insertion into the Zr-Me bonds formed by such an exchange. The abundance of iso-propyl groups, as measured from the well-resolved signals at 11.48 and 23.73 ppm, is 0.72 per 98 steroregular main-chain units (integrals estimated for an unresolved iso-propyl signal at 21.51 ppm (0.72, vide supra) and for the mmmr pentad at 21.40 ppm (1.34 = [mmrr]) have to be subtracted from the main signal at 21.69 ppm).

For n-propyl chain starts an abundance of 0.39 per 98 main-chain units is estimated from the signals at 14.38 and 19.70 ppm. Based on this estimate, the n-propyl signal at 20.70 ppm is too large. Apparently, it coincides with another signal close to it. For this signal, as for another signal observed at 20.03 ppm, no obvious assignments are apparent at this time.

The abundance of n-propyl chain starts, which arise either from propene insertion into Zr-H bonds generated by β-H transfer to the metal or from β-H transfer to a monomer, is normally equal to that of unsaturated chain ends, since either one of these processes produces a 2-propenyl end group. In the present polymer, however, unsaturated chain ends are hardly detectable at all from ^{13}C NMR spectra, while the ^{1}H NMR spectrum indicates an abundance of ca. 0.073 H_2C=C groups per 98 main-chain units, i.e. ca. 5 times less than n-propyl chain starts. Apparently, a substantial fraction of chains start by propene insertion into Zr-H bonds, which are derived from residual H-Al units still present is the reaction system, rather than from β-H transfer, while the growth of almost all chains is eventually terminated by transfer from Zr to Al.

A mean degree of polymerization, P_n = 45, corresponds to the number-average molar mass M_n = 1,873, obtained together with a value of PDI = 2.10 from a GPC analysis of this polymer sample (Figure S-11).

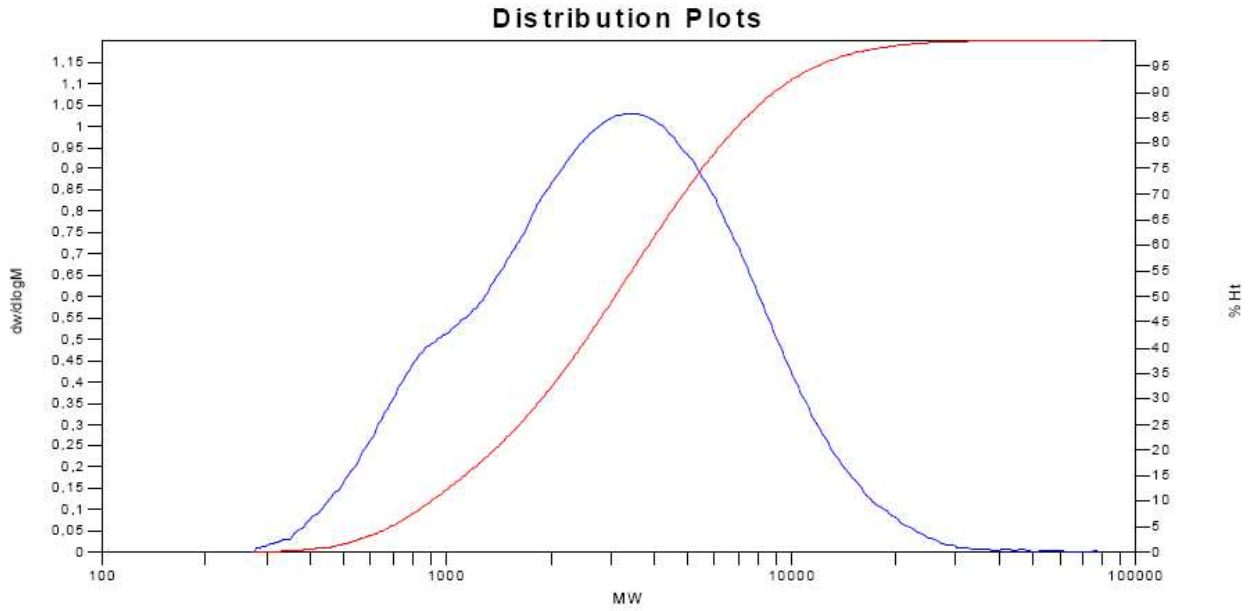

Figure S-11: GPC trace of polymer sample prepared with a mixture of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ and $AlMe_3$

1) Marvich, R. H.; Brintzinger, H. H. *J. Am. Chem. Soc*. **1971**, *93*, 2046.

2) Baldwin, S. M.; Bercaw, J. E.; Henling, L. M.; Day, M. W.; Brintzinger, H. H. *submitted*